



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

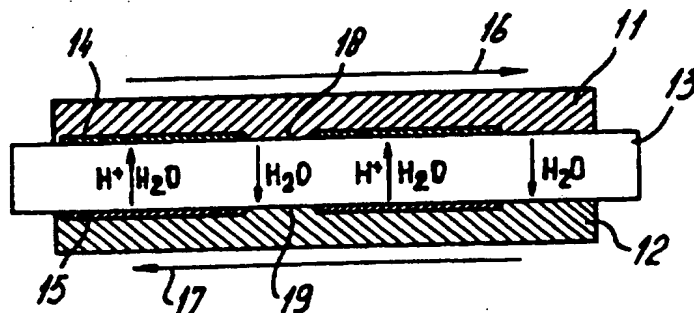
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : H01M 8/04, 8/10		A1	(11) International Publication Number: WO 96/24958
			(43) International Publication Date: 15 August 1996 (15.08.96)
(21) International Application Number: PCT/NL96/00063		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KG, KZ, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 9 February 1996 (09.02.96)			
(30) Priority Data: 9500253 10 February 1995 (10.02.95) NL			
(71) Applicant (for all designated States except US): STICHTING ENERGIEONDERZOEK CENTRUM [NL/NL]; Westerduinweg 3, NL-1755 LE Petten (NL).			
(72) Inventor; and (75) Inventor/Applicant (for US only): MALLANT, Ronald, Karel, Antoine, Maria [NL/NL]; Koggewaard 83, NL-1824 GP Alkmaar (NL).			
(74) Agent: DE BRUIJN, Leendert, C.; Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).		Published With international search report. In English translation (filed in Dutch).	

(54) Title: SOLID POLYMER FUEL CELL COMPRISING HUMIDITY-EXCHANGING AREAS

(57) Abstract

For the purpose of humidifying anode gases (17) with the aid of moisture present or in cathode gases (16) taken up it is proposed that the gases, in the cell or in the direct vicinity thereof, be caused to enter a humidity-exchanging relationship. In the case of the method being implemented in the cell, the anode (12) and the cathode (11) are designated as strips provided with catalyst (14, 15) and the areas (18, 19) inbetween as portions which are not provided with catalyst. These portions not provided with catalyst, which are non-active or less active, provide for optimal water permeability.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

Solid polymer fuel cell comprising
humidity-exchanging areas

5 The present invention relates to a solid polymer fuel cell, comprising an anode, electrolyte/diaphragm and cathode, and a supply and exhaust of gases on both the anode and the cathode side, the anode comprising areas provided with catalyst for carrying out the electrochemical reaction and, adjacent thereto, areas not provided with catalyst for absorbing moisture via electrolyte/diaphragm.

10 Such a device is known from US Patent No. 4,973,530.

It is necessary for anode gases, in particular, to be humidified, in order to keep the polymer/electrolyte sufficiently moist, so that optimal ion conductivity in the cell can occur and the latter thus has an adequate output. This is because, during operation of a solid polymer fuel cell, the transport of H^+ is accompanied, simultaneously, with the transport of water in the same direction. Although the phenomenon of water molecules being carried along by protons is compensated for, to some extent, by a diffusion of water molecules back to the anode, depletion of water takes place at the anode side of the cell with a corresponding poor conductivity for protons and a decrease in the output and performance of the cell.

20 The abovementioned US Patent No. 4,973,530 proposes to cause the gases to cover a serpentine trajectory across the electrode in question. The electrode which is provided with catalyst is bordered by an area which is not provided with electrolyte material, but where a water-exchanging diaphragm is present. Since the serpentine always covers a portion of the area where the water-exchanging diaphragm is present, it is possible for water to be taken up at the anode side. The converse process takes place at the cathode side, water being given off via a water-exchanging membrane and a water-absorbing medium.

35 It will be understood that at the anode side, based on this supply of water in the direction of the cell up to the point where the serpentine again reaches the water supply, the water concentration will decrease. Thus, a kind of sawtooth-like profile of the moisture concentration in the cell will be obtained. As a result, performance and output will have a corresponding profile.

The drawback of such cells is the presence of serpentine

which require expensive separate processing steps.

In the embodiment according to said US Patent, four different mass flows are present: the anode gas, the cathode gas, the medium (water) for humidifying the anode gas, and the medium
5 for removing the water from the cathode gas. These mass flows need to be kept separate from one another in a reliable manner.

Moreover, the medium which has removed the water from the cathode gas stream should be stripped of water, before said water can be passed through the humidifying sections of the anode
10 stream. This requires further expensive provisions.

The object of the present invention is to provide a fuel cell wherein such a serpentine supply or exhaust of gases is unnecessary and which can therefore be accomplished in a simple manner. Moreover, the depletion in terms of water vapour should be
15 compensated for at each point of the electrode and not just at one point.

This object is achieved, in an above-described solid polymer fuel cell, in that the areas provided with catalyst comprise strips which are bounded, at least on their long sides,
20 by areas not provided with catalyst, which areas without catalyst have a minimum width of 1 mm.

By virtue of the portions provided with catalyst being designed as strips which are bordered by non-active or less active portions as a result of the absence of catalyst, provision is
25 effectively made, at each point of the active portion of the electrode, for compensation of the depletion in moisture by water molecules being carried along together with H^+ .

It should be noted that the Japanese Patent Abstract No. 58-126675 discloses the use of a platinum mesh disposed on the diaphragm. Such a mesh is used to increase vibration resistance.
30 Although this publication does not give any dimensions, it can be assumed, presuming that the thickness of the membrane is between 100 and 200 μm , that the spacing of the platinum wires is in the order of 50 μm , in contrast to the present invention where the
35 spacing between the areas provided with catalyst is at least 1 mm. If the spacing is as small as shown in the "Abstract" of the Japanese Application No. 58-126675, the effect of certain areas not being active is not produced, and that entire portion of the diaphragm which is covered with platinum gauze, should be regarded

as one active area for the electrochemical reaction.

The European Application No. 0 654 837 A1, published after the priority date of the present application, proposes a saving in catalyst. In this case, the supply of gases takes place via corrugations, and where the corrugations touch the electrodes, the gases will be less active. Precisely at those points, less catalyst is applied. This, however, requires the accurate positioning, on top of one another, of the areas which are not provided with catalyst and of the corrugation. Moreover, in such areas it will also not be possible to move water back to the anode side, because of the obstructing portion of the corrugation.

The above-described design is of particular importance at the anode side because it is there that water depletion takes place.

However, it has proved to be advantageous for the cathode side to be designed in the same manner.

In order to optimize, as far as possible, the effect of water being moved back, the gas supply at the anode and the cathode, respectively, is preferably positioned so as not to be parallel to the strips in question. More in particular, it is perpendicular to the strips. The strips may be straight but may likewise be of any shape known in the prior art, such as a zigzag shape.

The invention also relates to a method for fabricating an above-described anode and/or cathode. In the process, there are provided a support not provided with catalyst and a slurry comprising carbon and catalyst, the slurry being applied to the support or to the polymer/electrolyte, in the desired pattern, by printing.

Of course, it is also possible to use other methods to apply the pattern in question to a support or to the polymer/electrolyte. By means of the invention the advantage is achieved that the cathode gases and anode gases enter a direct humidity-exchanging relationship, without use being made of water-separating facilities which are customarily incorporated in the cathode exhaust gas stream, without means for transferring said water to chambers which enter into a humidity-exchanging relationship with the anode gases, and without the need for compartments incorporated in the cell or in the immediate vicinity thereof and

intended to enable humidity exchange with cathode gas or anode gas.

Thus, it is possible for the catalyst (slurry) to be applied to the support or directly to the polymer, the support then being positioned against the polymer electrolyte provided with catalyst.

The invention is explained below in more detail with reference to the illustrative embodiments shown in the drawing, in which

Fig. 1 shows diagrammatically, in section, an SPFC cell, humidity exchange between cathode and anode gases taking place at the edge of the cell,

Fig. 2 shows, on a reduced scale, the entire cell according to Fig. 1 in top view;

Fig. 3 shows a second embodiment of the invention in section, exchange of humidity taking place in the cell;

Fig. 4 shows a top view, on a reduced scale, of the cell according to Fig. 3; and

Fig. 5 shows a top view of a variation of the embodiment according to Figs. 3 and 4.

Fig. 1 schematically depicts a detail of a solid polymer fuel cell. Only those parts are shown, which are important for understanding the present invention.

This cell is composed of a cathode 1 and an anode 2 between which a polymer diaphragm/electrolyte 3 is inserted. The cathode and anode are provided with catalyst, respectively indicated by 4 and 5. Arrow 6 indicates the motion of the oxygen-containing gas stream, whereas arrow 7 shows the movement of the fuel gas. It should be understood that both gases are passed over the electrodes via some sort of duct system. Likewise it should be understood that the indicated direction of movement of anode gases and cathode gases should be seen as preferred directions for obtaining an optimum result, but that other directions likewise fall within the scope of the invention described herein. Moreover, the cell may be a stacked cell.

Fig. 1 shows that there is no catalyst near the edge of the fuel cell. There, the anode and cathode are non-active with respect to effecting proton transport and are particularly porous. The cathode gas, whose oxygen has been consumed in its entirety or

in part contains, near the edge, a very high proportion of water. Owing to the anode gas, represented by arrow 7, being relatively dry, diffusion of water through electrolyte 3 will take place. In Fig. 2, the embodiment according to Fig. 1 is shown in its entirety in a view reduced in size. This shows that the left-hand edge area is intended for the diffusion, whereas the right-hand portion comprises the fuel cell proper. In the left-hand edge portion, water will move from cathode 1 to anode 2 and in the right-hand edge portion in exactly the opposite way.

Fig. 3 shows a further alternative of the invention. In this figure, the movement of water is likewise represented schematically.

The cathode is indicated herein by 11, the anode by 12, the electrolyte by 13, the catalysts by 14 and 15, whereas the arrow for oxygen-containing gas is indicated by 16 and the arrow for fuel gas by 17. It is clear that this cell contains areas (indicated by 18 and 19) where there is no catalyst, i.e. which are non-active or less active.

This figure shows that in the areas which are active and provided with catalyst, transport of water takes place from the anode 12 to the cathode 11. This gives rise to humidification of the cathode gas and water depletion of the anode gas. In the non-active portions precisely the opposite transport takes place. Because no reaction takes place there, transport of water will be determined exclusively by a diffusion mechanism and will not be prevented by the flow of protons.

By situating such non-active areas in the cell it is possible to provide, even in situ enrichment with water. As Fig. 3 shows, continuous humidification of the anode gases takes place and it is not necessary to add separate installations for removing the humidity from the cathode gas.

It should be understood that the figures are not drawn to scale. The thickness of the diaphragm 3 and 13, respectively, is usually in the range between 25 and 200 μm . The thickness of the electrodes is approximately 00 [sic]-400 μm .

Fig. 4 shows a top view of the cathode on a reduced scale. This shows that a series of areas which are less active alternates with a series of areas or strips which are active. The width of an active strip can be between 6 and 10 mm, whereas the

width of the portion not provided with catalyst is greater than 1 mm and is preferably 2 to 3 mm. Generally it can be assumed that the ratio not covered with catalyst/covered is $1/5 - 1/3$. Thus the distance which the water has to cover can be made as short as possible. In order, moreover, to make the design as robust as possible and achieve further optimization, the design according to Fig. 5 can be applied, in which 20 indicates the active areas.

It will be understood that the design shown in Figs. 4 and 5 obviously, and in the first instance, also applies to the anode side.

Although it has been stated, in the above, that the intended transport of humidity from cathode back to anode can be achieved by simply omitting the catalyst, this can be realised with any method known in the prior art. Thus it is possible for the electrode, in the areas in question, to be removed in its entirety.

The design shown with reference to Figs. 1-5 can be applied to each cell or a series of cells.

The above-described pattern of strips provided with catalyst and strips not provided with catalyst can be applied to the electrode in any manner known in the prior art. Preferably, printing is employed, since the slurry used for the catalyst can be adapted in a simple manner so as to have rheological properties comparable with printing ink. Thus, printing can be effected in a simple, accurate manner. This printing can take place with any method known in the prior art, such as screen printing, rotary printing and jet printing.

It was found that if, with respect to the active area, the non-active area having a surface area of 20% of the active area is used, sufficient recovery of water can be obtained to obviate additional installations. If required, separate means such as cavities may be present to collect the water and to redistribute it. Moreover, it is possible for the active and non-active areas to be completely separate from one another and to be situated at some distance from one another. The feature essential for the invention, which is that the cathode gases serve as a humidity (water) carrier, is maintained in such an embodiment.

These and other variations are deemed to be within the scope of the accompanying claims.

Claims

1. Solid polymer fuel cell, comprising an anode (12), electrolyte/diaphragm (13) and cathode (11), and a supply and exhaust of gases on both the anode and the cathode side, the anode comprising areas provided with catalyst (15) for carrying out the electrochemical reaction and, adjacent thereto, areas (19) not provided with catalyst for absorbing moisture via electrolyte/diaphragm, characterized in that said areas provided with catalyst comprise strips which are bounded, at least on their long sides, by areas not provided with catalyst, which areas without catalyst have a minimum width of 1 mm.
2. Solid polymer fuel cell according to Claim 1, the cathode comprising areas provided with catalyst for carrying out the electrochemical reaction and, adjacent thereto, areas not provided with catalyst for giving off moisture via the electrolyte/diaphragm, wherein said areas provided with catalyst comprise strips which are bounded, at least on their long sides, by areas not provided with catalyst, which areas without catalyst have a minimum width of 1 mm.
3. Solid polymer fuel cell (SPFC), wherein the gas supply takes place at the anode and/or cathode at an angle with said strips.
4. Solid polymer fuel cell according to Claim 3, wherein the gas supply takes place at the anode and/or cathode essentially perpendicular to said strips.
5. Solid polymer fuel cell, wherein said strips are designed in a zigzag shape.
6. Solid polymer fuel cell according to any one of the preceding claims, wherein the catalyst comprises platinum.
7. Method for fabricating an anode/cathode according to any one of the preceding claims, comprising the provision of a support not provided with catalyst and of a slurry comprising carbon and catalyst, wherein the suspension is applied to the support, in the desired pattern, by printing.

1/1

fig-1

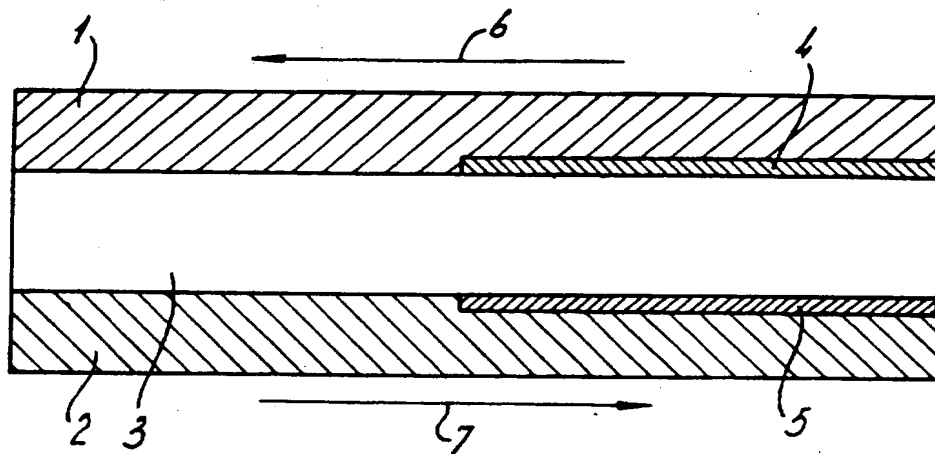


fig-2

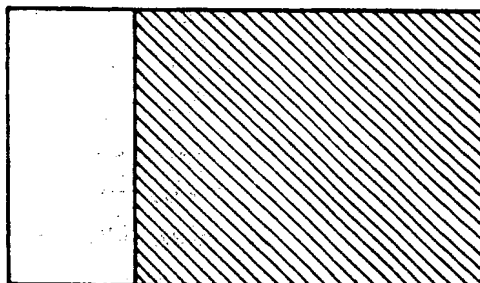


fig-3

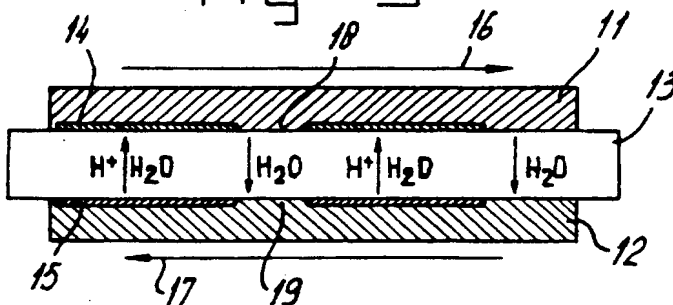


fig-4

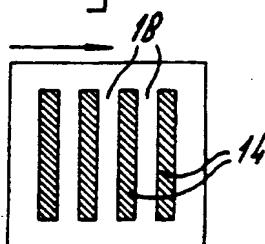
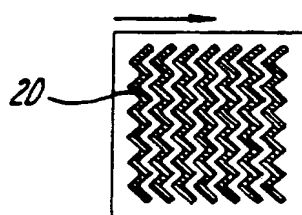


fig-5



INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/NL 96/00063

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01M8/04 H01M8/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 275 465 (DOW CHEMICAL CO) 27 July 1988 see column 16, line 1 - line 9; claims 1,2,4,15; figure 3 see column 6, line 4 - line 12 see column 8, line 43 - line 52 ---	1,2,6
X	DE,A,14 21 612 (SIEMENS AG) 20 February 1969 see page 5, line 14; claim 1; figures 1,2 ---	1,2,6
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 608 (E-1457), 9 November 1993 & JP,A,05 190184 (HONDA MOTOR CO LTD), 30 July 1993, see abstract --- -/-	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "A" document member of the same patent family

Date of the actual completion of the international search

24 May 1996

Date of mailing of the international search report

31.05.96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

D'hondt, J

INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/NL 96/00063

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AT,B,389 020 (SCHUETZ PETER DIPL ING DR) 10 October 1989 see page 2, last paragraph - page 3, paragraph 1 see page 3, paragraph 3 see page 5, line 15 - line 36 ---	1
A	FR,A,1 154 282 (GENERAL ELECTRIC COMPANY) 4 April 1958 see figure 1 ---	3,4
A	PATENT ABSTRACTS OF JAPAN vol. 008, no. 013 (E-222), 20 January 1984 & JP,A,58 176879 (KOGYO GIJUTSUIN;OTHERS: OJ), 17 October 1983, see abstract ---	3,4
P,X	EP,A,0 654 837 (JOHNSON MATTHEY PLC) 24 May 1995 cited in the application see page 5, line 27 - line 39; claims 1,11; examples 2,1 ---	7
P,A	---	1
A	EP,A,0 637 851 (MATSUSHITA ELECTRIC IND CO LTD) 8 February 1995 see page 4, line 54 - page 5, line 1; claim 2 ---	7
A	US,A,4 973 530 (VANDERBORGH NICHOLAS E ET AL) 27 November 1990 cited in the application see column 7, line 41 - line 58; claims 1,8; figure 2A 2B see column 8, line 25 - line 30; figures 4A,4B ---	1,2
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 308 (E-1560), 13 June 1994 & JP,A,06 068896 (FUJI ELECTRIC CO LTD), 11 March 1994, see abstract ---	1
A	WO,A,92 13365 (BALLARD POWER SYSTEMS INC) 6 August 1992 see page 4, line 2 - line 19 see page 6, line 9 - line 16 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/NL 96/00063

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0275465	27-07-88	US-A- 4738741 AU-B- 582318 AU-B- 8219987 DE-A- 3781262 JP-B- 1021231 JP-C- 1538401 JP-A- 63179089 US-A- 5039389	19-04-88 16-03-89 07-07-88 24-09-92 20-04-89 16-01-90 23-07-88 13-08-91
DE-A-1421612	20-02-69	NONE	
AT-B-389020	10-10-89	NONE	
FR-A-1154282	04-04-58	DE-B- 1036345 GB-A- 794471 US-A- 2913511	17-11-59
EP-A-0654837	24-05-95	CA-A- 2136133 JP-A- 7240204	24-05-95 12-09-95
EP-A-0637851	08-02-95	CA-A- 2127171 US-A- 5474857 JP-A- 7183035	07-02-95 12-12-95 21-07-95
US-A-4973530	27-11-90	NONE	
WO-A-9213365	06-08-92	US-A- 5260143 AU-B- 660446 AU-B- 1164292 EP-A- 0567499 JP-T- 6504403 US-A- 5441819 US-A- 5366818	09-11-93 29-06-95 27-08-92 03-11-93 19-05-94 15-08-95 22-11-94

THIS PAGE BLANK (US)